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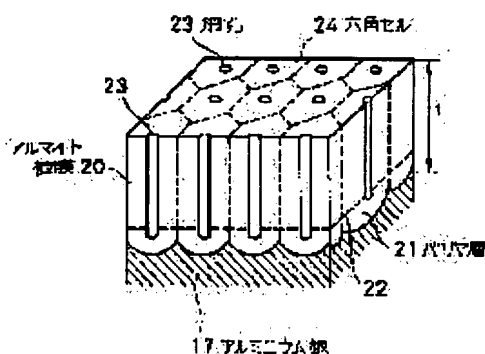
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## (54) ZINC-BROMINE BATTERY SEPARATOR AND ITS MANUFACTURE



(57)Abstract:

PURPOSE: To provide a zinc-bromine battery separator and its manufacture by which battery efficiency can be heightened by heightening the accuracy of the hole diameter control of the separator, and shortening a hole process.

CONSTITUTION: An anodic oxide coating formed by anodizing aluminum is used as a zinc-bromine battery separator. Oxalic acid, sulfuric acid, or liquid formed by adding sulfosalicylic acid to the sulfuric acid is used as electrolyte in a reaction vessel 15, and an aluminum plate 17 of 0.3mm or less in thickness is soaked in a positive electrode side and a lead electrode is soaked opposite thereto in a

negative electrode side. Anodizing is conducted as maintaining the temperature of the electrolyte, a power source voltage, and an electric current density at adequate values so as to form the anodic oxide coating 20 on the surface of the aluminum plate 17 to obtain the zinc-bromine battery separator.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the separator which is the configuration member of an electrolytic-solution cycloid type laminating rechargeable battery, especially a zinc-bromine cell, and its manufacture approach.

[0002]

[Description of the Prior Art] It is the rechargeable battery to which the zinc-bromine cell used the bromine for positive active material, and used zinc for the negative-electrode active material, and in order to make the daytime of power, and the imbalance of night solve this cell, it stores power in the night with few power requirements, and it is used in order to make it emit to day ranges.

[0003] The bromine generated in the positive-electrode electrode side at the time of charge reacts with the bromine complexing agent added to the electrolytic solution, it becomes oil-like precipitate and is returned to a storage tank, and with a pump, it is sent in into a cell at the time of discharge, and it is returned. The component of the electrolytic solution is with Pb for preventing ZnBr<sub>2</sub> water solution, salts for lowering resistance, such as NH<sub>4</sub>Cl, and the dendrite by the side of negative-electrode zinc, and promoting uniform electrodeposition, Sn, quarternary ammonium salt, and a bromine complexing agent. The separator is inserted between the positive-electrode electrode and the negative-electrode electrode, and the self-discharge by the bromine generated with the positive-electrode electrode being spread to a negative-electrode electrode, and reacting with zinc is prevented.

[0004] The chemical reaction of this zinc-bromine cell is [0005].

[Formula 1]

the time of charge .... positive-electrode:  $2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$  and negative-electrode:  $\text{Zn}^{++} + 2\text{e}^- \rightarrow \text{Zn}$  the time of discharge .. positive-electrode: -- it is expressed with  $2\text{Br}^- \leftarrow \text{Br}_2 + 2\text{e}^-$  and negative-electrode:  $\text{Zn}^{++} + 2\text{e}^- \leftarrow \text{Zn}$ .

[0006] This zinc-bromine cell consists of a cell proper which mainly used the electrode as the bipolar mold and carried out the laminating of two or more cells (single cel) to the serial electrically, an electrolytic-solution storage tank, and the pump and the pipe line which circulate the electrolytic solution among these.

[0007] The working principle of a zinc-bromine cell is explained based on the schematic diagram of drawing 6 . One in drawing is a positive-electrode side storage tank, and the positive-electrode electrolytic solution 2 and the bromine complex compound 3 are stored in this positive-electrode side storage tank 1. 4 is a negative-electrode side storage tank, and the negative-electrode electrolytic solution 5 is stored in this negative-electrode side storage tank 4. And while the positive-electrode electrolytic solution 2 circulates the positive-electrode interior of a room from

the positive-electrode manifold 8 of a cell proper with actuation of the positive-electrode side pump 6 as shown in the arrow head in drawing through the four-way valve 7, and flowing back to the positive-electrode side storage tank 1, the negative-electrode electrolytic solution 5 circulates the negative-electrode interior of a room separated from the negative-electrode manifold 10 of a cell proper by the separator 11 with actuation of the negative-electrode side pump 9, and flows back to the negative-electrode side storage tank 4. 12 is a bipolar electrode and 13 is a current collection electrode.

[0008] After the electrode material of the current collection electrode 13 carries out melting mixing of the carbon black and graphite for giving conductivity by using polyethylene as a binder by the proper ratio, the sheet-sized carbon plastics electrode material is used for it. In order to decrease the reaction overvoltage of a bromine to a positive electrode, what sheet-sized the carbon cross or the carbon fiber with the resin binder is made to have laminated.

[0009] After carrying out melting mixing of a silica and the dioctyl phthalate (DOP), and extracting and porosity-izing DOP to polyethylene resin with the above-mentioned usually comparatively hard separator 11 with a solvent, the \*\*\*\* porous membrane obtained with an extrusion-molding means is used for it. The average aperture of this fine porous membrane serves as about 0.1-micrometer (1000Å) extent.

[0010] The above-mentioned zinc-bromine cell reacts with the bromine complexing agent (quarternary ammonium salt) with which the bromine generated in the positive-electrode side at the time of charge is contained in the electrolytic solution, it is stored by the bottom of a positive-electrode side tank as oil-like bromine complex, the bromine which is not complex-ized serves as  $\text{Br}_3$ -ion, it dissolves in the electrolytic solution, and electrocrystallization of the zinc is carried out to a carbon plastics electrode.

[0011] Thus, about 70% is checked as total energy efficiency about 80% as cell effectiveness [ in / in the constituted zinc-bromine cell / 50kW class cell ].

[0012]

[Problem(s) to be Solved by the Invention] The effectiveness of such a zinc-bromine cell for stationary energy storage has the problem of aperture control of a separator in one of the factors which check effectiveness, although it is required that overall efficiency also including inverter effectiveness should be raised. As described above, a separator is porous membrane, and even if it penetrates  $\text{Zn}^{++}$  ion and  $\text{Br}$ -ion, a bromine and a bromine complex compound need not to penetrate. When especially an aperture is too large, a bromine molecule ( $\text{Br}_2$ ) and a bromine complex compound ( $\text{QBr}_3$ ) will also be penetrated so much, and the effectiveness of a cell will fall.

[0013] however, the hole which penetrated detailed aperture control in the shape of a straight line by the fixed aperture difficultly by the approach of carrying out extrusion molding after the aperture of this separator changing with process conditions in many cases and carrying out melting mixing of the silica with DOP at usual polyethylene resin -- the problem that a configuration is not acquired remains and it is in the difficult actual condition to obtain the good separator of permselectivity which was described above.

[0014] Usually, although the aperture of the separator using polyethylene resin is an average of 0.1 micrometers (1000Å), about 200-500Å is actually imagined to be a suitable thing. Moreover, since the hole has penetrated between the front flesh sides of a separator plate in the complicated path so that between voids may be sewn, it is usually that the actual stroke of a hole is quite longer than board thickness. Furthermore, for a certain reason, the thickness of a separator plate is in the inclination which swelling of the electrolytic solution in a cell tends to generate also

about 1mm.

[0015] While this invention is made in view of the above-mentioned point and raising the precision of aperture control of said separator, it aims at offering the separator for zinc-bromine cells which can shorten a actual stroke and can raise cell effectiveness, and its manufacture approach by forming a hole in the shape of a straight line.

[0016]

[Means for Solving the Problem] In order to attain the above-mentioned object, while this invention forms a single cel in a bipolar electrode for a separator in piles, carries out the laminating of two or more these single cels and constitutes a cell proper It is characterized by using the alumite coat formed in the both ends of this cell proper by carrying out anodizing of the aluminum as said separator in the zinc-bromine cell which arranges the current collection electrode and the end plate with a bundle of a couple, and was made to carry out laminating immobilization in one.

[0017] As claim 2, the oxalic acid whose concentration is 3 - 4% as the electrolytic solution is put in in a reaction vessel. While board thickness is immersed in an anode plate side in an aluminum plate 0.3mm or less, a lead electrode is immersed in a cathode side face to face, and while connecting the plus side of a power source to aluminum, the minus side of a power source is connected to a lead electrode. It anodizes by maintaining the temperature of the electrolytic solution, supply voltage, and current density to a proper value, and the manufacture approach of the separator for zinc-bromine cells in which the alumite coat was formed on the surface of the aluminum plate is offered.

[0018] By separating the alumite coat formed on the above-mentioned aluminum plate of claim 3 from right above [ barrier layer ] with a reverse-current peeling method, the porosity alumite coat which has the hexagon-head cel which much pores penetrated is obtained, and the approach which heat-treated preferably 850 degrees C or more of this alumite coat at 900 degrees C of abbreviation in atmospheric air for 1 hour is offered.

[0019] Furthermore, the approach using the liquid which added the sulfosalicylic acid for the approach using the sulfuric acid which contains an aluminum sulfate as the electrolytic solution by claim 4 to the sulfuric acid as the electrolytic solution by claim 5 is offered.

[0020] Moreover, the mask with which opening of many round holes was carried out to the field which should anodize an aluminum plate is fixed by claim 6. An alumite coat is formed in the surface part of the aluminum plate which is not covered with a mask by anodizing in the electrolytic solution. Furthermore, form an alumite coat the whole surface from hard flow, and this alumite coat is connected with the field which the above-mentioned alumite coat of an aluminum plate formed with said alumite coat. Dissolution clearance of the unreacted aluminum plate which remains into the part covered with the mask is carried out using an acid, each flat side is connected back to back using two sheets of the obtained member, and the manufacture approach of the separator for zinc-bromine cells of having fixed and obtained the electrode plate to both sides is offered.

[0021]

[Function] According to this separator, by carrying out anodizing of the aluminum plate, a porous alumite coat is formed and the porosity alumite coat which the pore of a large number which distributed this to homogeneity in the direction of board thickness by dissociating from an aluminum plate side right above [ of a barrier layer ] with a reverse-current peeling method etc. penetrated is obtained. Since the size of pore is determined by the electrical potential difference applied to a coat at the time of the above-mentioned anodic oxidation, control of a pole diameter

becomes easy.

[0022] An alumite [ having carried out anodizing ] coat is aluminum  $2O_3$  of an amorphous condition, by heat-treating after anodic oxidation, it metamorphoses into the crystal structure of delta-aluminum  $2O_3$ , and its corrosion resistance in the inside of the electrolytic solution of strong acid nature also improves substantially.

[0023] Pore has penetrated this alumite coat in the shape of a straight line in the direction of board thickness, and the same board thickness of the stroke of a hole is also quite short as compared with the usual porosity polyethylene film. And thickness of an alumite coat can be substantially made thin.

[0024] Furthermore, by having used the approach according to claim 6, while the separator itself is miniaturized, the good film of permselectivity is obtained, and as compared with the kneading activity of conventional polyethylene resin, manufacture can obtain the easy separator for zinc-bromine cells.

[0025]

[Example] The various concrete examples of the separator for zinc-bromine cells which starts this invention below, and its manufacture approach are explained. In this example, it has been the big description to have used the alumite coat formed by carrying out anodizing of the aluminum as a separator which has permselectivity.

[0026] Drawing 2 is the example of anodic oxidation equipment of the aluminum adopted in the 1st example of this invention. As illustrated, oxalic acid 16 is put in as the electrolytic solution in a reaction vessel 15. To an anode plate side an aluminum plate 17 By making it react, connecting the minus side of a power source 19 to the lead electrode 18, and maintaining proper temperature and a proper electrical potential difference, while the lead electrode 18 is immersed in a cathode side face to face and connecting the plus side of a power source 19 to an aluminum plate 17 An anodic oxide film 20, i.e., an alumite coat, is formed in the front face of an aluminum plate 17.

[0027] In this example, as membrane formation conditions for the alumite coat 20 of the porosity by the describing [ above ] oxalic acid method, as for more than aluminum 99.99% and board thickness, the chemical composition of an aluminum plate 17 set to 0.3mm or less, and, as for the concentration of oxalic acid 16, the temperature of the electrolytic solution set 25V(DC) or 80V(AC), and current density to 100 (A/m<sup>2</sup>, DC) or 50 (A/m<sup>2</sup>, AC) for the electrical potential difference of 20 degrees C - 30 degrees C and a power source 19 3 to 4%.

[0028] Although the obtained alumite coat 20 was transparent in direct current voltage, it presented light yellow - brown in alternating voltage.

[0029] Drawing 1 is the schematic diagram showing the structure of the obtained porosity alumite coat 20, and thickness t which has the hexagon-head cel 24 which pores 23 and 23 penetrated up and down obtained 80 micrometers (a maximum of 400 micrometers) and a porosity alumite coat with a pore diameter of 40nm (400Å) by separating the alumite coat 20 formed on the aluminum plate 17 from an aluminum plate 17 side in the dotted-line section 22 of barrier layer 21 right above with a reverse-current peeling method. 900 degrees C of this alumite coat 20 were heat-treated in atmospheric air for 1 hour.

[0030] Therefore, in the \*\*\*\* 1 example, by carrying out anodizing of the aluminum plate 17 by the oxalic acid method, it is possible to grow up the porous alumite coat 20 to the thickness of a maximum of 400 micrometers, and the porosity alumite coat 20 to which much pores 23 and 23 penetrated this in the direction of board thickness by dissociating from an aluminum plate 17 side right above [ of a barrier layer 21 ] with a reverse-current peeling method etc. is obtained.

[0031] The size of the above-mentioned hexagon-head cel 24 and the size of pores 23 and 23 are

determined by the electrical potential difference applied to a coat at the time of the above-mentioned anodizing. When an electrical potential difference is set to V, the size diameter DC of the hexagon-head cell 24 (2R) is  $DC=23 \times V$  (A), and the size diameter DP of pores 23 and 23 (2r) is  $DP=DC/3$  (A).

[0032] The original form was held without dissolving, even if it is immersed into the electrolytic solution for strong acid nature cells of pH1 and carries out progress of the alumite coat 20 obtained by this example for 1500 hours (about two months).

[0033] Drawing 3 (A) and (B) are spectrums in which the analysis result by the X-ray diffraction of the alumite coat 20 obtained by this example is shown, and this drawing (A) heat-treats a non-heated thing and 900 degrees C (B) of these drawings in atmospheric air for 1 hour. The alumite [ having carried out anodizing from drawing 3 ] coat 20 is aluminum 2O3 of an amorphous condition, and it became clear by heat-treating after anodizing that it metamorphosed into the crystal structure of delta-aluminum 2O3.

[0034] Drawing 4 was a spectrum in which the thermogravimetric measurement (TG) result of the alumite coat 20 is shown, the weight gradual decrease by bleedoff of the moisture which was sticking to the coat front face in connection with the temperature rise from this drawing was accepted, and the large decrease of weight considered to correspond to a transformation into delta-aluminum 2O3 crystal from an amorphous condition near 850 degree C was accepted. This is considered to originate in decomposition bleedoff of the water of crystallization from a hydrate, or decomposition bleedoff of the OH radical from \*\*\*\*\* rare \*\*\*\*\* (OH) aluminum 3.

[0035] That is, it became clear by having adsorbed moisture that the alumite coat 20 which consists of aluminum 2O3 in the amorphous condition that water of crystallization and aluminum (OH)3 were included in part metamorphosed on delta-aluminum 2O3 crystal, and its corrosion resistance in the inside of the electrolytic solution of strong acid nature was also improving substantially by 900-degree C elevated-temperature heat-treatment.

[0036] although the aperture of the present porosity polyethylene film separator is an average of 0.1 micrometers (1000A), it is alike and compares, and with the electrical potential difference to apply, control of a pole diameter is possible for the alumite coat by the oxalic acid method within the limits of about 200A - 500A, and it becomes easy to control [ of this pole diameter ] it. The obtained pole diameter is also small and pore is distributing it to homogeneity.

[0037] Moreover, since pore has penetrated the alumite coat by the oxalic acid method in the shape of a straight line in the direction of board thickness, as compared with the present porosity polyethylene film, i.e., the film which pore has penetrated in the complicated path as sewed between many voids, the same board thickness of the stroke of a hole is also quite short.

[0038] Furthermore, an oxalic acid alumite coat can make board thickness thin substantially as compared with a porosity polyethylene coat. Coat creation of arbitration is possible for the thickness of the oxalic acid alumite coat of this example in about 30-400 micrometers to the thickness of the present polyethylene film being about 1mm.

[0039] Although the alumite coat which formed membranes according to \*\*\*\* 1 example will be dissolved in a short time on 2 or the 3rd in the electrolytic solution of strong acid nature by aluminum 2O3 in the amorphous condition that were easy to adsorb moisture and water of crystallization and aluminum (OH)3 were included in part, elevated-temperature heat-treatment of 1 hour is preferably carved at 900 degrees C, 850 degrees C or more metamorphose into delta-aluminum 2O3 crystal, and corrosion resistance can be improved substantially. However, in a single alumite coat, large-area-izing is difficult and about 5x5cm is usually a limitation.

[0040] Next, the 2nd example of this invention is explained. In this 2nd example, it is

characterized by having replaced with the oxalic acid as the electrolytic solution used when forming an alumite coat in said 1st example, and using a sulfuric acid. In addition, other parts are the same only by the anodic oxidation equipment of the aluminum shown in drawing 2 changing oxalic acid 16 into a sulfuric acid. The aluminum sulfate of the specified quantity contains in this sulfuric acid.

[0041] As membrane formation conditions for the porosity alumite coat 20 by this sulfuric-acid method, chemical composition of an aluminum plate 17 was made more than aluminum 99.99%, board thickness made to 0.3mm or less, and, in the temperature of 1-50 (kg/m<sup>3</sup>), and the electrolytic solution, 15-20V (DC), and current density set [ the concentration of the sulfuric acid as the electrolytic solution / the aluminum sulfate ] 15 degrees C - 25 degrees C and supply voltage to 80-300 (A/m<sup>2</sup>) 5 to 25%. The alumite coat 20 obtained by this sulfuric-acid method presented colorless transparency.

[0042] The structure of the porosity alumite coat 20 obtained in the 2nd example is the same as that of drawing 1 , and thickness t which has the hexagon-head cel 24 which pores 23 and 23 penetrated up and down obtained the porosity alumite coat in the range which is 30 micrometers - 300 micrometers and the pole diameter of 100A - 250A by dissociating from an aluminum plate 17 side in the dotted-line section 22 of barrier layer 21 right above with a reverse-current peeling method. 900 degrees C of this alumite coat 20 were heat-treated in atmospheric air for 1 hour.

[0043] The original form was held without dissolving, even if it is the same as that of said example 1 that the size of the above-mentioned hexagon-head cel 24 and the size of pores 23 and 23 are determined, and it is immersed into the electrolytic solution for strong acid nature cells of pH1 and carries out progress of the obtained alumite coat 20 for 1500 hours ( about two months) with the electrical potential difference applied to a coat at the time of anodizing.

[0044] When the analysis result by the X-ray diffraction of the alumite coat 20 obtained in this 2nd example was seen, the alumite [ having carried out anodizing ] coat 20 is aluminum 2O<sub>3</sub> of an amorphous condition, and it became clear by heat-treating after anodizing that it metamorphosed into the crystal structure of delta-aluminum 2O<sub>3</sub>. Furthermore, according to the spectrum in which a thermogravimetric measurement (TG) result is shown, the weight gradual decrease by bleedoff of the moisture which was sticking to the coat front face in connection with the temperature rise was accepted, and the large decrease of weight considered to correspond to a transformation into delta-aluminum 2O<sub>3</sub> crystal from an amorphous condition near 890 degree C was accepted.

[0045] Next, the 3rd example of this invention is explained. In this 3rd example, in case an alumite coat is created, it is characterized by using the cull color method. By this cull color method, the liquid which added the sulfosalicylic acid 100 (kg/m<sup>3</sup>) is used for the sulfuric acid 50 (kg/m<sup>3</sup>) as the electrolytic solution, and, in the temperature of the electrolytic solution, 25-70V (DC), and current density set 22 degrees C - 25 degrees C and supply voltage to 200-3200 (A/m<sup>2</sup>). The alumite coat 20 obtained by this cull color method presented bronze - black.

[0046] In addition, other parts are the same only by the anodic oxidation equipment of the aluminum shown in drawing 2 changing the electrolytic solution. As membrane formation conditions for the porosity alumite coat 20 by this cull color method, more than aluminum 99.99% and board thickness could be 0.3mm or less as chemical composition of an aluminum plate 17.

[0047] The structure of the obtained porosity alumite coat 20 is the same as that of drawing 1 , and thickness t which has the hexagon-head cel 24 which pores 23 and 23 penetrated up and down obtained the porosity alumite coat which are 30 micrometers - 400 micrometers and the

pole diameter of 200A - 600A by dissociating from an aluminum plate 17 side in the dotted-line section 22 of barrier layer 21 right above with a reverse-current peeling method. 900 degrees C of this alumite coat 20 were heat-treated in atmospheric air for 1 hour.

[0048] The original form was held without dissolving, even if it is the same as that of said example 1 that the size of the above-mentioned hexagon-head cell 24 and the size of pores 23 and 23 are determined, and it is immersed into the electrolytic solution for strong acid nature cells of pH1 and carries out progress of the obtained alumite coat 20 for 1500 hours ( about two months) with the electrical potential difference applied to a coat at the time of anodizing.

[0049] When the analysis result by the X-ray diffraction of the alumite coat 20 obtained in this 3rd example was seen, the alumite [ having carried out anodizing ] coat 20 is aluminum 2O3 of an amorphous condition, and it became clear by heat-treating after anodizing that it metamorphosed into the crystal structure of delta-aluminum 2O3. Furthermore, according to the spectrum in which a thermogravimetric measurement (TG) result is shown, the weight gradual decrease by bleedoff of the moisture which was sticking to the coat front face in connection with the temperature rise was accepted, and the large decrease of weight considered to correspond to a transformation into delta-aluminum 2O3 crystal from an amorphous condition near 860 degree C was accepted.

[0050] Drawing 5 shows the 5th example of this invention, and this example shows the example which manufactured the separator 11 for zinc-bromine cells using the formation approach of the alumite coat 20 explained in each above-mentioned example.

[0051] If it explains based on the order of a process below, the mask 25 with which opening of many round holes was carried out to the field which should anodize the aluminum plate 17 with a thickness of 0.8mm first as shown in this drawing (A) will be fixed. It sets to the pars basilaris ossis occipitalis of a reaction vessel 15 as an anode plate by making into the inside the field which this mask 25 fixed. While putting in oxalic acid 16 as the electrolytic solution, opposite arrangement of the lead electrode 18 is carried out at a cathode side, and while connecting the plus side of a power source 19 to aluminum 17, the minus side of a power source 19 is connected to the lead electrode 18. And if an anodic oxidation reaction is made to perform, maintaining the temperature, the electrical potential difference, and current density which were indicated in said 1st example, the alumite coats 20 and 20 will be formed in the surface part of the aluminum plate 17 which is not covered with a mask 25. In addition, thickness of these alumite coats 20 and 20 is set to 0.4mm.

[0052] Next, as shown in this drawing (B), the upper and lower sides of an aluminum plate 17 are reversed, and alumite coat 20a is formed in the whole surface based on the actuation same from hard flow as the field in which the above-mentioned alumite coat 20 was formed. Thickness of this alumite coat 20a is set to 0.4mm like the above.

[0053] Since the islands 17a and 17a of unreacted aluminum remain in the part in which the alumite coat 20 and alumite coat 20a connected from the upper and lower sides, and were covered with this process with the mask 25, the whole is immersed in the container 28 which filled the hydrochloric acid 27 as shown in this drawing (C), and dissolution clearance of the unreacted aluminum plate 17 is carried out. 26 is the clearance part of aluminum and the part which makes the alumite coats 20 and 20a a subject remains in a hydrochloric acid 27, without dissolving. In addition, it is immersed in a sodium-hydroxide solution next, and a barrier layer is removed.

[0054] This drawing (D) and (E) show the structure of the separator 11 constituted by the obtained alumite coat, connect two flat sides of both members back to back using the member



which consisted of alumite coats 20 and 20a obtained by the above, fix the electrode plates 29 and 29 to right-and-left both sides, and are completed to them. At this time, the hole section 30 serves as passage of the electrolytic solution.

[0055] According to this 5th example, while separator 11 the very thing is miniaturized, the good film of permselectivity is obtained, and the process itself is simplified as compared with the kneading activity of conventional polyethylene resin, and manufacture can obtain the easy separator for zinc-bromine cells.

[0056]

[Effect of the Invention] As explained to the detail above, according to the separator for zinc-bromine cells concerning this invention Since the size of pore is determined by the electrical potential difference applied to a coat at the time of anodic oxidation by having realized the separator made from the porous alumite coat obtained by carrying out anodizing of the aluminum plate the hole which the precision of the detailed aperture control of a separator set to one of the factors which control of a pore diameter becomes easy and prevent cell effectiveness from the former improved, and was penetrated in the shape of a straight line by the fixed aperture -- a configuration is acquired, permselectivity is good and the separator which can raise cell effectiveness is obtained.

[0057] Since the above-mentioned pore is distributed to homogeneity in the direction of board thickness and it has moreover penetrated in the shape of a straight line, the same board thickness also becomes quite short [ the stroke of a hole ] as compared with the usual porosity polyethylene film, and thickness of an alumite coat can be substantially made thin.

[0058] Furthermore, by having used the approach according to claim 6, while the separator itself is miniaturized, as compared with the kneading activity of conventional polyethylene resin, manufacture can obtain the easy separator for zinc-bromine cells.

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## TECHNICAL FIELD

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[Industrial Application] This invention relates to the separator which is the configuration member of an electrolytic-solution cycloid type laminating rechargeable battery, especially a zinc-bromine cell, and its manufacture approach.

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## PRIOR ART

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[Description of the Prior Art] It is the rechargeable battery to which the zinc-bromine cell used the bromine for positive active material, and used zinc for the negative-electrode active material, and in order to make the daytime of power, and the imbalance of night solve this cell, it stores power in the night with few power requirements, and it is used in order to make it emit to day ranges.

[0003] The bromine generated in the positive-electrode electrode side at the time of charge reacts with the bromine complexing agent added to the electrolytic solution, it becomes oil-like precipitate and is returned to a storage tank, and with a pump, it is sent in into a cell at the time of discharge, and it is returned. The component of the electrolytic solution is with Pb for preventing  $ZnBr_2$  water solution, salts for lowering resistance, such as  $NH_4Cl$ , and the dendrite by the side of negative-electrode zinc, and promoting uniform electrodeposition, Sn, quarternary ammonium salt, and a bromine complexing agent. The separator is inserted between the positive-electrode electrode and the negative-electrode electrode, and the self-discharge by the bromine

generated with the positive-electrode electrode being spread to a negative-electrode electrode, and reacting with zinc is prevented.

[0004] The chemical reaction of this zinc-bromine cell is [0005].

[Formula 1]

the time of charge .... positive-electrode:  $2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$  and negative-electrode:  $\text{Zn} \rightarrow \text{Zn}^{++} + 2\text{e}^-$   
the time of discharge .. positive-electrode:  $2\text{Br}^- \leftarrow \text{Br}_2 + 2\text{e}^-$  and negative-electrode:  $\text{Zn}^{++} + 2\text{e}^- \leftarrow \text{Zn}$ .

[0006] This zinc-bromine cell consists of a cell proper which mainly used the electrode as the bipolar mold and carried out the laminating of two or more cells (single cel) to the serial electrically, an electrolytic-solution storage tank, and the pump and the pipe line which circulate the electrolytic solution among these.

[0007] The working principle of a zinc-bromine cell is explained based on the schematic diagram of drawing 6 . One in drawing is a positive-electrode side storage tank, and the positive-electrode electrolytic solution 2 and the bromine complex compound 3 are stored in this positive-electrode side storage tank 1. 4 is a negative-electrode side storage tank, and the negative-electrode electrolytic solution 5 is stored in this negative-electrode side storage tank 4. And while the positive-electrode electrolytic solution 2 circulates the positive-electrode interior of a room from the positive-electrode manifold 8 of a cell proper with actuation of the positive-electrode side pump 6 as shown in the arrow head in drawing through the four-way valve 7, and flowing back to the positive-electrode side storage tank 1, the negative-electrode electrolytic solution 5 circulates the negative-electrode interior of a room separated from the negative-electrode manifold 10 of a cell proper by the separator 11 with actuation of the negative-electrode side pump 9, and flows back to the negative-electrode side storage tank 4. 12 is a bipolar electrode and 13 is a current collection electrode.

[0008] After the electrode material of the current collection electrode 13 carries out melting mixing of the carbon black and graphite for giving conductivity by using polyethylene as a binder by the proper ratio, the sheet-ized carbon plastics electrode material is used for it. In order to decrease the reaction overvoltage of a bromine to a positive electrode, what sheet-ized the carbon cross or the carbon fiber with the resin binder is made to have laminated.

[0009] After carrying out melting mixing of a silica and the dioctyl phthalate (DOP), and extracting and porosity-izing DOP to polyethylene resin with the above-mentioned usually comparatively hard separator 11 with a solvent, the \*\*\*\* porous membrane obtained with an extrusion-molding means is used for it. The average aperture of this fine porous membrane serves as about 0.1-micrometer (1000Å) extent.

[0010] The above-mentioned zinc-bromine cell reacts with the bromine complexing agent (quaternary ammonium salt) with which the bromine generated in the positive-electrode side at the time of charge is contained in the electrolytic solution, it is stored by the bottom of a positive-electrode side tank as oil-like bromine complex, the bromine which is not complex-ized serves as  $\text{Br}_3^-$ -ion, it dissolves in the electrolytic solution, and electrocrystallization of the zinc is carried out to a carbon plastics electrode.

[0011] Thus, about 70% is checked as total energy efficiency about 80% as cell effectiveness [ in / in the constituted zinc-bromine cell / 50kW class cell ].

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## EFFECT OF THE INVENTION

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[Effect of the Invention] As explained to the detail above, according to the separator for zinc-bromine cells concerning this invention Since the size of pore is determined by the electrical potential difference applied to a coat at the time of anodic oxidation by having realized the separator made from the porous alumite coat obtained by carrying out anodizing of the aluminum plate the hole which the precision of the detailed aperture control of a separator set to one of the factors which control of a pore diameter becomes easy and prevent cell effectiveness from the former improved, and was penetrated in the shape of a straight line by the fixed aperture -- a configuration is acquired, permselectivity is good and the separator which can raise cell effectiveness is obtained.

[0057] Since the above-mentioned pore is distributed to homogeneity in the direction of board thickness and it has moreover penetrated in the shape of a straight line, the same board thickness also becomes quite short [ the stroke of a hole ] as compared with the usual porosity polyethylene film, and thickness of an alumite coat can be substantially made thin.

[0058] Furthermore, by having used the approach according to claim 6, while the separator itself is miniaturized, as compared with the kneading activity of conventional polyethylene resin, manufacture can obtain the easy separator for zinc-bromine cells.

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## TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] The effectiveness of such a zinc-bromine cell for stationary energy storage has the problem of aperture control of a separator in one of the factors which check effectiveness, although it is required that overall efficiency also including inverter effectiveness should be raised. As described above, a separator is porous membrane, and even if it penetrates  $Zn^{++}$  ion and Br-ion, a bromine and a bromine complex compound need not to penetrate. When especially an aperture is too large, a bromine molecule ( $Br_2$ ) and a bromine complex compound ( $QBr_3$ ) will also be penetrated so much, and the effectiveness of a cell will fall.

[0013] however, the hole which penetrated detailed aperture control in the shape of a straight line by the fixed aperture difficultly by the approach of carrying out extrusion molding after the aperture of this separator changing with process conditions in many cases and carrying out melting mixing of the silica with DOP at usual polyethylene resin -- the problem that a configuration is not acquired remains and it is in the difficult actual condition to obtain the good separator of permselectivity which was described above.

[0014] Usually, although the aperture of the separator using polyethylene resin is an average of 0.1 micrometers (1000A), about 200-500A is actually imagined to be a suitable thing. Moreover, since the hole has penetrated between the front flesh sides of a separator plate in the complicated path so that between voids may be sewn, it is usually that the actual stroke of a hole is quite longer than board thickness. Furthermore, for a certain reason, the thickness of a separator plate is in the inclination which swelling of the electrolytic solution in a cell tends to generate also about 1mm.

[0015] While this invention is made in view of the above-mentioned point and raising the precision of aperture control of said separator, it aims at offering the separator for zinc-bromine cells which can shorten a actual stroke and can raise cell effectiveness, and its manufacture approach by forming a hole in the shape of a straight line.

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## MEANS

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[Means for Solving the Problem] In order to attain the above-mentioned object, while this invention forms a single cel in a bipolar electrode for a separator in piles, carries out the laminating of two or more these single cels and constitutes a cell proper It is characterized by using the alumite coat formed in the both ends of this cell proper by carrying out anodizing of the aluminum as said separator in the zinc-bromine cell which arranges the current collection electrode and the end plate with a bundle of a couple, and was made to carry out laminating immobilization in one.

[0017] As claim 2, the oxalic acid whose concentration is 3 - 4% as the electrolytic solution is put in in a reaction vessel. While board thickness is immersed in an anode plate side in an aluminum plate 0.3mm or less, a lead electrode is immersed in a cathode side face to face, and while connecting the plus side of a power source to aluminum, the minus side of a power source is connected to a lead electrode. It anodizes by maintaining the temperature of the electrolytic solution, supply voltage, and current density to a proper value, and the manufacture approach of the separator for zinc-bromine cells in which the alumite coat was formed on the surface of the aluminum plate is offered.

[0018] By separating the alumite coat formed on the above-mentioned aluminum plate of claim 3 from right above [ barrier layer ] with a reverse-current peeling method, the porosity alumite coat which has the hexagon-head cel which much pores penetrated is obtained, and the approach which heat-treated preferably 850 degrees C or more of this alumite coat at 900 degrees C of abbreviation in atmospheric air for 1 hour is offered.

[0019] Furthermore, the approach using the liquid which added the sulfosalicylic acid for the approach using the sulfuric acid which contains an aluminum sulfate as the electrolytic solution by claim 4 to the sulfuric acid as the electrolytic solution by claim 5 is offered.

[0020] Moreover, the mask with which opening of many round holes was carried out to the field which should anodize an aluminum plate is fixed by claim 6. An alumite coat is formed in the surface part of the aluminum plate which is not covered with a mask by anodizing in the electrolytic solution. Furthermore, form an alumite coat the whole surface from hard flow, and this alumite coat is connected with the field which the above-mentioned alumite coat of an aluminum plate formed with said alumite coat. Dissolution clearance of the unreacted aluminum plate which remains into the part covered with the mask is carried out using an acid, each flat side is connected back to back using two sheets of the obtained member, and the manufacture approach of the separator for zinc-bromine cells of having fixed and obtained the electrode plate to both sides is offered.

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## OPERATION

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[Function] According to this separator, by carrying out anodizing of the aluminum plate, a porous alumite coat is formed and the porosity alumite coat which the pore of a large number which distributed this to homogeneity in the direction of board thickness by dissociating from an aluminum plate side right above [ of a barrier layer ] with a reverse-current peeling method etc. penetrated is obtained. Since the size of pore is determined by the electrical potential difference applied to a coat at the time of the above-mentioned anodic oxidation, control of a pole diameter becomes easy.

[0022] An alumite [ having carried out anodizing ] coat is aluminum 2O3 of an amorphous condition, by heat-treating after anodic oxidation, it metamorphoses into the crystal structure of

delta-aluminum  $2O_3$ , and its corrosion resistance in the inside of the electrolytic solution of strong acid nature also improves substantially.

[0023] Pore has penetrated this alumite coat in the shape of a straight line in the direction of board thickness, and the same board thickness of the stroke of a hole is also quite short as compared with the usual porosity polyethylene film. And thickness of an alumite coat can be substantially made thin.

[0024] Furthermore, by having used the approach according to claim 6, while the separator itself is miniaturized, the good film of permselectivity is obtained, and as compared with the kneading activity of conventional polyethylene resin, manufacture can obtain the easy separator for zinc-bromine cells.

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## EXAMPLE

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[Example] The various concrete examples of the separator for zinc-bromine cells which starts this invention below, and its manufacture approach are explained. In this example, it has been the big description to have used the alumite coat formed by carrying out anodizing of the aluminum as a separator which has permselectivity.

[0026] Drawing 2 is the example of anodic oxidation equipment of the aluminum adopted in the 1st example of this invention. As illustrated, oxalic acid 16 is put in as the electrolytic solution in a reaction vessel 15. To an anode plate side an aluminum plate 17 By making it react, connecting the minus side of a power source 19 to the lead electrode 18, and maintaining proper temperature and a proper electrical potential difference, while the lead electrode 18 is immersed in a cathode side face to face and connecting the plus side of a power source 19 to an aluminum plate 17 An anodic oxide film 20, i.e., an alumite coat, is formed in the front face of an aluminum plate 17.

[0027] In this example, as membrane formation conditions for the alumite coat 20 of the porosity by the describing [ above ] oxalic acid method, as for more than aluminum 99.99% and board thickness, the chemical composition of an aluminum plate 17 set to 0.3mm or less, and, as for the concentration of oxalic acid 16, the temperature of the electrolytic solution set 25V(DC) or 80V(AC), and current density to 100 (A/m<sup>2</sup>, DC) or 50 (A/m<sup>2</sup>, AC) for the electrical potential difference of 20 degrees C - 30 degrees C and a power source 19 3 to 4%.

[0028] Although the obtained alumite coat 20 was transparent in direct current voltage, it presented light yellow - brown in alternating voltage.

[0029] Drawing 1 is the schematic diagram showing the structure of the obtained porosity alumite coat 20, and thickness t which has the hexagon-head cel 24 which pores 23 and 23 penetrated up and down obtained 80 micrometers (a maximum of 400 micrometers) and a porosity alumite coat with a pore diameter of 40nm (400Å) by separating the alumite coat 20 formed on the aluminum plate 17 from an aluminum plate 17 side in the dotted-line section 22 of barrier layer 21 right above with a reverse-current peeling method. 900 degrees C of this alumite coat 20 were heat-treated in atmospheric air for 1 hour.

[0030] Therefore, in the \*\*\*\* 1 example, by carrying out anodizing of the aluminum plate 17 by the oxalic acid method, it is possible to grow up the porous alumite coat 20 to the thickness of a maximum of 400 micrometers, and the porosity alumite coat 20 to which much pores 23 and 23 penetrated this in the direction of board thickness by dissociating from an aluminum plate 17 side right above [ of a barrier layer 21 ] with a reverse-current peeling method etc. is obtained.

[0031] The size of the above-mentioned hexagon-head cel 24 and the size of pores 23 and 23 are determined by the electrical potential difference applied to a coat at the time of the above-

mentioned anodizing. When an electrical potential difference is set to  $V$ , the size diameter  $DC$  of the hexagon-head cell 24 (2R) is  $DC=23 \times V$  (A), and the size diameter  $DP$  of pores 23 and 23 (2r) is  $DP=DC/3$  (A).

[0032] The original form was held without dissolving, even if it is immersed into the electrolytic solution for strong acid nature cells of pH1 and carries out progress of the alumite coat 20 obtained by this example for 1500 hours (about two months).

[0033] Drawing 3 (A) and (B) are spectrums in which the analysis result by the X-ray diffraction of the alumite coat 20 obtained by this example is shown, and this drawing (A) heat-treats a non-heated thing and 900 degrees C (B) of these drawings in atmospheric air for 1 hour. The alumite [ having carried out anodizing from drawing 3 ] coat 20 is aluminum  $2O_3$  of an amorphous condition, and it became clear by heat-treating after anodizing that it metamorphosed into the crystal structure of delta-aluminum  $2O_3$ .

[0034] Drawing 4 was a spectrum in which the thermogravimetric measurement (TG) result of the alumite coat 20 is shown, the weight gradual decrease by bleedoff of the moisture which was sticking to the coat front face in connection with the temperature rise from this drawing was accepted, and the large decrease of weight considered to correspond to a transformation into delta-aluminum  $2O_3$  crystal from an amorphous condition near 850 degree C was accepted. This is considered to originate in decomposition bleedoff of the water of crystallization from a hydrate, or decomposition bleedoff of the OH radical from \*\*\*\*\* rare \*\*\*\*\* (OH) aluminum 3.

[0035] That is, it became clear by having adsorbed moisture that the alumite coat 20 which consists of aluminum  $2O_3$  in the amorphous condition that water of crystallization and aluminum (OH) $_3$  were included in part metamorphosed on delta-aluminum  $2O_3$  crystal, and its corrosion resistance in the inside of the electrolytic solution of strong acid nature was also improving substantially by 900-degree C elevated-temperature heat-treatment.

[0036] although the aperture of the present porosity polyethylene film separator is an average of 0.1 micrometers (1000A), it is alike and compares, and with the electrical potential difference to apply, control of a pole diameter is possible for the alumite coat by the oxalic acid method within the limits of about 200A - 500A, and it becomes easy to control [ of this pole diameter ] it. The obtained pole diameter is also small and pore is distributing it to homogeneity.

[0037] Moreover, since pore has penetrated the alumite coat by the oxalic acid method in the shape of a straight line in the direction of board thickness, as compared with the present porosity polyethylene film, i.e., the film which pore has penetrated in the complicated path as sewed between many voids, the same board thickness of the stroke of a hole is also quite short.

[0038] Furthermore, an oxalic acid alumite coat can make board thickness thin substantially as compared with a porosity polyethylene coat. Coat creation of arbitration is possible for the thickness of the oxalic acid alumite coat of this example in about 30-400 micrometers to the thickness of the present polyethylene film being about 1mm.

[0039] Although the alumite coat which formed membranes according to \*\*\*\* 1 example will be dissolved in a short time on 2 or the 3rd in the electrolytic solution of strong acid nature by aluminum  $2O_3$  in the amorphous condition that were easy to adsorb moisture and water of crystallization and aluminum (OH) $_3$  were included in part, elevated-temperature heat-treatment of 1 hour is preferably carved at 900 degrees C, 850 degrees C or more metamorphose into delta-aluminum  $2O_3$  crystal, and corrosion resistance can be improved substantially. However, in a single alumite coat, large-area-izing is difficult and about 5x5cm is usually a limitation.

[0040] Next, the 2nd example of this invention is explained. In this 2nd example, it is characterized by having replaced with the oxalic acid as the electrolytic solution used when

forming an alumite coat in said 1st example, and using a sulfuric acid. In addition, other parts are the same only by the anodic oxidation equipment of the aluminum shown in drawing 2 changing oxalic acid 16 into a sulfuric acid. The aluminum sulfate of the specified quantity contains in this sulfuric acid.

[0041] As membrane formation conditions for the porosity alumite coat 20 by this sulfuric-acid method, chemical composition of an aluminum plate 17 was made more than aluminum 99.99%, board thickness made to 0.3mm or less, and, in the temperature of 1-50 (kg/m<sup>3</sup>), and the electrolytic solution, 15-20V (DC), and current density set [ the concentration of the sulfuric acid as the electrolytic solution / the aluminum sulfate ] 15 degrees C - 25 degrees C and supply voltage to 80-300 (A/m<sup>2</sup>) 5 to 25%. The alumite coat 20 obtained by this sulfuric-acid method presented colorless transparency.

[0042] The structure of the porosity alumite coat 20 obtained in the 2nd example is the same as that of drawing 1 , and thickness t which has the hexagon-head cel 24 which pores 23 and 23 penetrated up and down obtained the porosity alumite coat in the range which is 30 micrometers - 300 micrometers and the pole diameter of 100A - 250A by dissociating from an aluminum plate 17 side in the dotted-line section 22 of barrier layer 21 right above with a reverse-current peeling method. 900 degrees C of this alumite coat 20 were heat-treated in atmospheric air for 1 hour.

[0043] The original form was held without dissolving, even if it is the same as that of said example 1 that the size of the above-mentioned hexagon-head cel 24 and the size of pores 23 and 23 are determined, and it is immersed into the electrolytic solution for strong acid nature cells of pH1 and carries out progress of the obtained alumite coat 20 for 1500 hours ( about two months) with the electrical potential difference applied to a coat at the time of anodizing.

[0044] When the analysis result by the X-ray diffraction of the alumite coat 20 obtained in this 2nd example was seen, the alumite [ having carried out anodizing ] coat 20 is aluminum 2O<sub>3</sub> of an amorphous condition, and it became clear by heat-treating after anodizing that it metamorphosed into the crystal structure of delta-aluminum 2O<sub>3</sub>. Furthermore, according to the spectrum in which a thermogravimetric measurement (TG) result is shown, the weight gradual decrease by bleedoff of the moisture which was sticking to the coat front face in connection with the temperature rise was accepted, and the large decrease of weight considered to correspond to a transformation into delta-aluminum 2O<sub>3</sub> crystal from an amorphous condition near 890 degree C was accepted.

[0045] Next, the 3rd example of this invention is explained. In this 3rd example, in case an alumite coat is created, it is characterized by using the cull color method. By this cull color method, the liquid which added the sulfosalicylic acid 100 (kg/m<sup>3</sup>) is used for the sulfuric acid 50 (kg/m<sup>3</sup>) as the electrolytic solution, and, in the temperature of the electrolytic solution, 25-70V (DC), and current density set 22 degrees C - 25 degrees C and supply voltage to 200-3200 (A/m<sup>2</sup>). The alumite coat 20 obtained by this cull color method presented bronze - black.

[0046] In addition, other parts are the same only by the anodic oxidation equipment of the aluminum shown in drawing 2 changing the electrolytic solution. As membrane formation conditions for the porosity alumite coat 20 by this cull color method, more than aluminum 99.99% and board thickness could be 0.3mm or less as chemical composition of an aluminum plate 17.

[0047] The structure of the obtained porosity alumite coat 20 is the same as that of drawing 1 , and thickness t which has the hexagon-head cel 24 which pores 23 and 23 penetrated up and down obtained the porosity alumite coat which are 30 micrometers - 400 micrometers and the pole diameter of 200A - 600A by dissociating from an aluminum plate 17 side in the dotted-line

section 22 of barrier layer 21 right above with a reverse-current peeling method. 900 degrees C of this alumite coat 20 were heat-treated in atmospheric air for 1 hour.

[0048] The original form was held without dissolving, even if it is the same as that of said example 1 that the size of the above-mentioned hexagon-head cel 24 and the size of pores 23 and 23 are determined, and it is immersed into the electrolytic solution for strong acid nature cells of pH1 and carries out progress of the obtained alumite coat 20 for 1500 hours ( about two months) with the electrical potential difference applied to a coat at the time of anodizing.

[0049] When the analysis result by the X-ray diffraction of the alumite coat 20 obtained in this 3rd example was seen, the alumite [ having carried out anodizing ] coat 20 is aluminum 2O3 of an amorphous condition, and it became clear by heat-treating after anodizing that it metamorphosed into the crystal structure of delta-aluminum 2O3. Furthermore, according to the spectrum in which a thermogravimetric measurement (TG) result is shown, the weight gradual decrease by bleedoff of the moisture which was sticking to the coat front face in connection with the temperature rise was accepted, and the large decrease of weight considered to correspond to a transformation into delta-aluminum 2O3 crystal from an amorphous condition near 860 degree C was accepted.

[0050] Drawing 5 shows the 5th example of this invention, and this example shows the example which manufactured the separator 11 for zinc-bromine cells using the formation approach of the alumite coat 20 explained in each above-mentioned example.

[0051] If it explains based on the order of a process below, the mask 25 with which opening of many round holes was carried out to the field which should anodize the aluminum plate 17 with a thickness of 0.8mm first as shown in this drawing (A) will be fixed. It sets to the pars basilaris ossis occipitalis of a reaction vessel 15 as an anode plate by making into the inside the field which this mask 25 fixed. While putting in oxalic acid 16 as the electrolytic solution, opposite arrangement of the lead electrode 18 is carried out at a cathode side, and while connecting the plus side of a power source 19 to aluminum 17, the minus side of a power source 19 is connected to the lead electrode 18. And if an anodic oxidation reaction is made to perform, maintaining the temperature, the electrical potential difference, and current density which were indicated in said 1st example, the alumite coats 20 and 20 will be formed in the surface part of the aluminum plate 17 which is not covered with a mask 25. In addition, thickness of these alumite coats 20 and 20 is set to 0.4mm.

[0052] Next, as shown in this drawing (B), the upper and lower sides of an aluminum plate 17 are reversed, and alumite coat 20a is formed in the whole surface based on the actuation same from hard flow as the field in which the above-mentioned alumite coat 20 was formed. Thickness of this alumite coat 20a is set to 0.4mm like the above.

[0053] Since the islands 17a and 17a of unreacted aluminum remain in the part in which the alumite coat 20 and alumite coat 20a connected from the upper and lower sides, and were covered with this process with the mask 25, the whole is immersed in the container 28 which filled the hydrochloric acid 27 as shown in this drawing (C), and dissolution clearance of the unreacted aluminum plate 17 is carried out. 26 is the clearance part of aluminum and the part which makes the alumite coats 20 and 20a a subject remains in a hydrochloric acid 27, without dissolving. In addition, it is immersed in a sodium-hydroxide solution next, and a barrier layer is removed.

[0054] This drawing (D) and (E) show the structure of the separator 11 constituted by the obtained alumite coat, connect two flat sides of both members back to back using the member which consisted of alumite coats 20 and 20a obtained by the above, fix the electrode plates 29



and 29 to right-and-left both sides, and are completed to them. At this time, the hole section 30 serves as passage of the electrolytic solution.

[0055] According to this 5th example, while separator 11 the very thing is miniaturized, the good film of permselectivity is obtained, and the process itself is simplified as compared with the kneading activity of conventional polyethylene resin, and manufacture can obtain the easy separator for zinc-bromine cells.

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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] The schematic diagram showing the structure of the porosity alumite coat obtained by this example.

[Drawing 2] The outline sectional view showing the example of anodic oxidation equipment of the aluminum adopted by this example.

[Drawing 3] The spectrum in which the analysis result by the X-ray diffraction of the alumite coat obtained by this example is shown.

[Drawing 4] The spectrum in which the thermogravimetric measurement (TG) result of the alumite coat obtained by this example is shown.

[Drawing 5] The schematic diagram showing the example which manufactured the separator for zinc-bromine cells using the formation approach of the alumite coat concerning this example.

[Drawing 6] The schematic diagram explaining the working principle of a zinc-bromine cell.

[Description of Notations]

- 1 -- Positive-electrode side storage tank
- 2 -- Positive-electrode electrolytic solution
- 3 -- Bromine complex compound
- 4 -- Negative-electrode side storage tank
- 5 -- Negative-electrode electrolytic solution
- 6 -- Positive-electrode side pump
- 7 -- Four-way valve
- 8 -- Positive-electrode manifold
- 9 -- Negative-electrode manifold
- 11 -- Separator
- 12 -- Bipolar electrode
- 13 -- Current collection electrode
- 15 -- Reaction vessel
- 16 -- Oxalic acid
- 17 -- Aluminum plate
- 18 -- Lead electrode
- 19 -- Power source
- 20 -- Alumite coat
- 21 -- Barrier layer
- 23 -- Pore
- 24 -- Hexagon-head cel
- 25 -- Mask
- 29 -- Electrode plate

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## CLAIMS

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### [Claim(s)]

[Claim 1] While forming a single cel in a bipolar electrode for a separator in piles, carrying out the laminating of two or more these single cels and constituting a cell proper In the zinc-bromine cell which arranges the current collection electrode and the end plate with a bundle of a couple to the both ends of this cell proper, and was made to carry out laminating immobilization in one The separator for zinc-bromine cells characterized by using the alumite coat formed by carrying out anodizing of the aluminum as said separator.

[Claim 2] While putting in the oxalic acid whose concentration is 3 - 4% as the electrolytic solution in a reaction vessel and immersing board thickness in an anode plate side in an aluminum plate 0.3mm or less, a lead electrode is immersed in a cathode side face to face. While connecting the plus side of a power source to aluminum, the minus side of a power source is connected to a lead electrode. 20 degrees C - 30 degrees C and supply voltage for the temperature of the electrolytic solution 25V(DC) or 80V(AC), The manufacture approach of the separator for zinc-bromine cells characterized by having anodized considering current density as 100 (A/m<sup>2</sup>, DC) or 50 (A/m<sup>2</sup>, AC), and forming an alumite coat on the surface of an aluminum plate.

[Claim 3] The manufacture approach of the separator for zinc-bromine cells according to claim 2 characterize by having obtain the porosity alumite coat which have the hexagon head cel which much pores penetrated by separate the alumite coat formed on the above-mentioned aluminum plate from right above [ barrier layer ] with a reverse-current peeling method, and heat-treat this alumite coat above 850 degrees C in atmospheric air for abbreviation 1 hour.

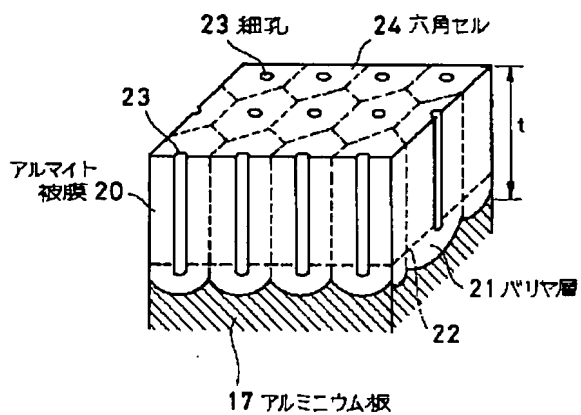
[Claim 4] The manufacture approach of the separator for zinc-bromine cells characterized by having anodized the concentration of this sulfuric acid in the aluminum sulfate 5 to 25% by having set 15-20V (DC), and current density to 80-300 (A/m<sup>2</sup>) for supply voltage, having set 1-50 (kg/m<sup>3</sup>), and temperature as 15 degrees C - 25 degrees C, and forming an alumite coat on the surface of an aluminum plate while using the sulfuric acid which contains an aluminum sulfate as the electrolytic solution.

[Claim 5] The manufacture approach of the separator for zinc-bromine cells characterized by having anodized by having set 25-70V (DC), and current density to 200-3200 (A/m<sup>2</sup>) for supply voltage, having set temperature of the electrolytic solution as 22 degrees C - 25 degrees C, and forming an alumite coat on the surface of an aluminum plate while using the liquid which added the sulfosalicylic acid to the sulfuric acid as the electrolytic solution.

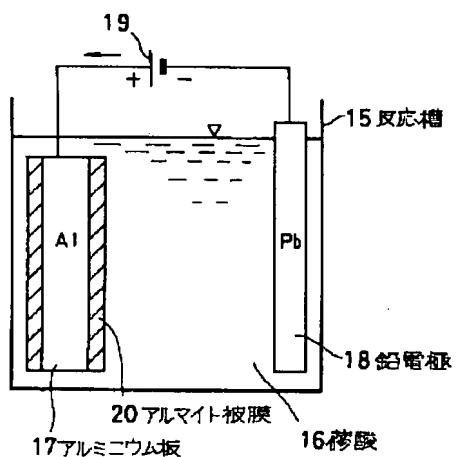
[Claim 6] The mask with which opening of many round holes was carried out to the field which should anodize an aluminum plate is fixed. An alumite coat is formed in the surface part of the aluminum plate which is not covered with a mask by anodizing in the electrolytic solution. Furthermore, form an alumite coat the whole surface from hard flow, and this alumite coat is connected with the field which the above-mentioned alumite coat of an aluminum plate formed with said alumite coat. The manufacture approach of the separator for zinc-bromine cells characterized by having carried out dissolution clearance of the unreacted aluminum plate which remains into the part covered with the mask using the acid, having connected each flat side back to back using two sheets of the obtained member, and fixing and obtaining an electrode plate to both sides.

# DRAWINGS

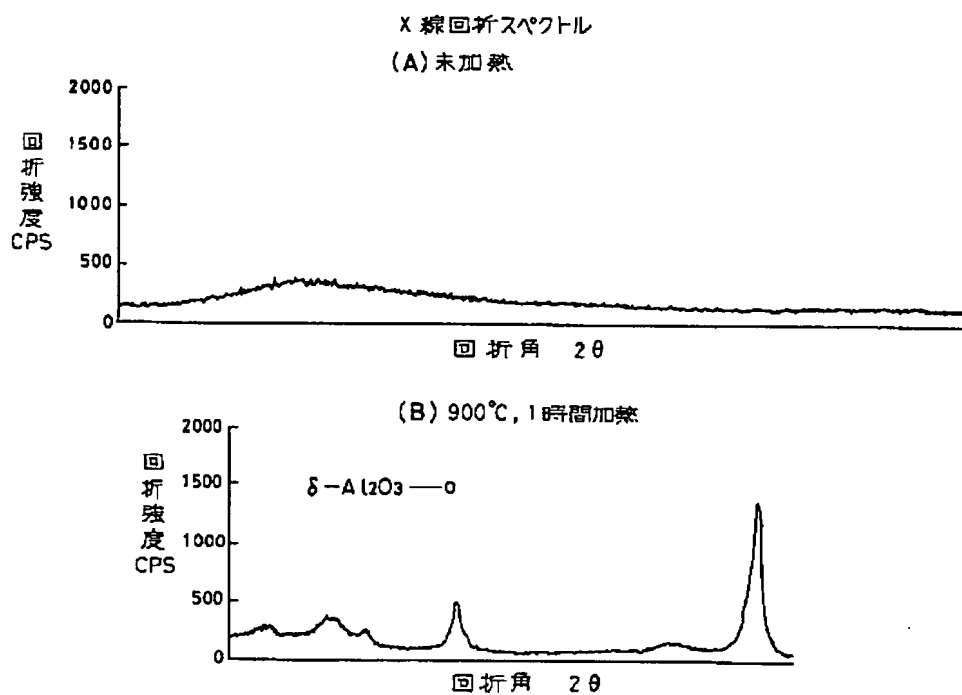
[Drawing 1]



[Drawing 2]

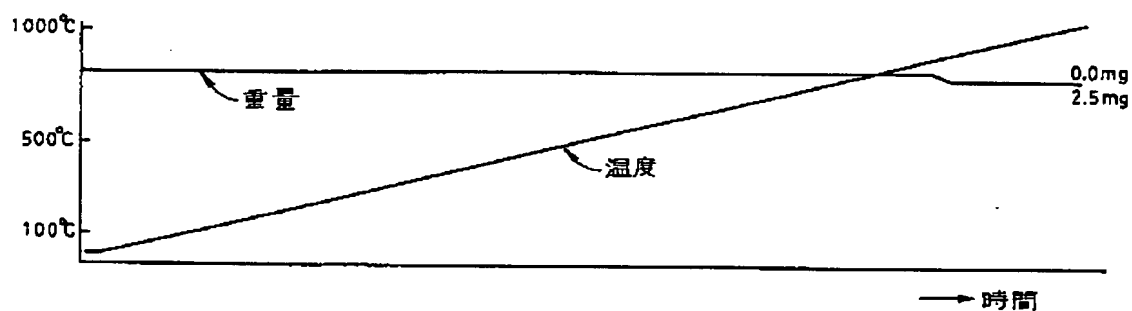


[Drawing 3]



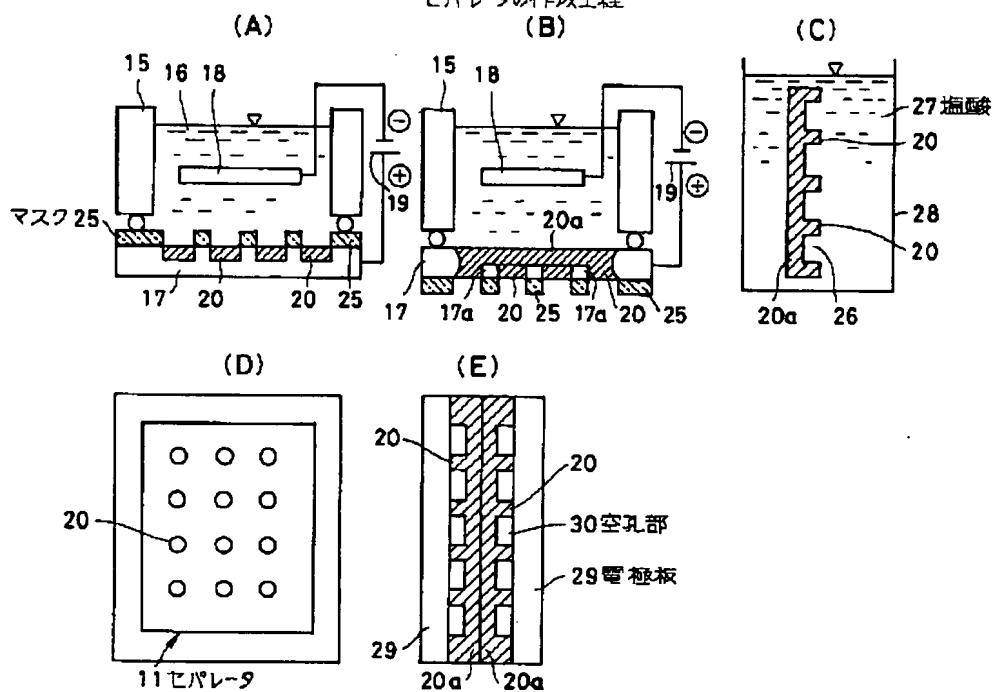
[Drawing 4]

熱重量測定 (TG) スペクトル

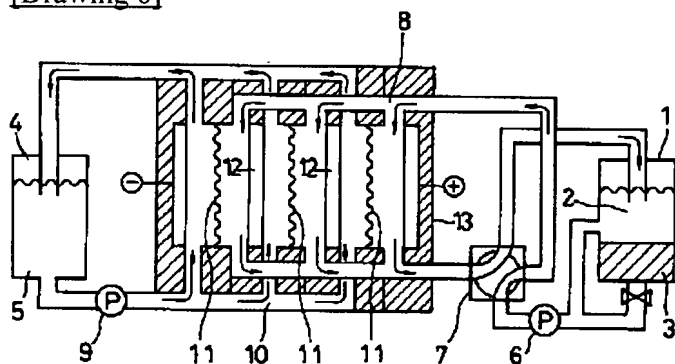


[Drawing 5]

セパレータの作製工程



[Drawing 6]



- 1 …正極側貯蔵槽
- 2 …正極電解液
- 3 …臭素錯化合物
- 4 …負極側貯蔵槽
- 5 …負極電解液
- 7 …四方弁
- 8 …正極マニホールド
- 9 …負極マニホールド
- 11 …セパレータ
- 12 …中間電極
- 13 …集電電極

[Translation done.]

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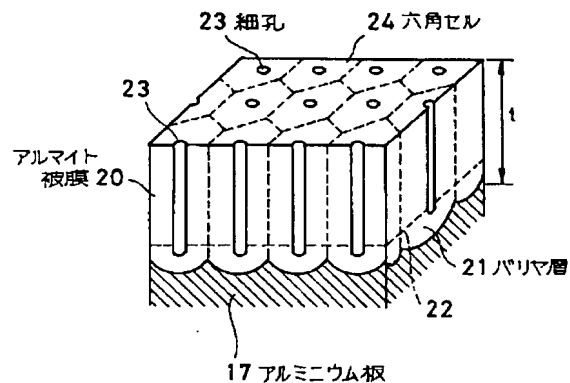
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(54) 【発明の名称】 亜鉛-臭素電池用セパレータ及びその製造方法

## (57) 【要約】

【目的】 セパレータの孔径制御の精度を高め、孔の行程を短縮して電池効率を高めることができる亜鉛-臭素電池用セパレータとその製造方法を提供することを目的とする。

【構成】 亜鉛-臭素電池用セパレータとして、アルミニウムを陽極酸化処理することによって形成されるアルマイト皮膜を用いる。セパレータの製法は、反応槽内15に電解液として稀酸、硫酸又は硫酸にスルホサリチル酸を加えた液を用いて、陽極側に板厚が0.3mm以下のアルミニウム板17を浸漬するとともに陰極側に鉛電極を対向して浸漬して、電解液の温度、電源電圧、電流密度を適宜な値に維持して陽極酸化を行い、アルミニウム板17の表面にアルマイト皮膜20を形成した亜鉛-臭素電池用セパレータの製造方法を提供する。



## 【特許請求の範囲】

【請求項 1】 中間電極にセパレータを重ねて単セルを形成し、この単セルを複数個積層して電池本体を構成するとともに、該電池本体の両端部に一對の集電電極と締付端板を配置して一体的に積層固定するようにした亜鉛-臭素電池において、

前記セパレータとして、アルミニウムを陽極酸化処理することによって形成されるアルマイト皮膜を用いたことを特徴とする亜鉛-臭素電池用セパレータ。

【請求項 2】 反応槽内に電解液として濃度が 3～4 % の稀酸を入れ、陽極側に板厚が 0.3 mm 以下のアルミニウム板を浸漬するとともに陰極側に鉛電極を対向して浸漬し、電源のプラス側をアルミニウムに接続するとともに電源のマイナス側を鉛電極に接続して、電解液の温度を 20℃～30℃、電源電圧を 25 V (DC) 又は 80 V (AC)、電流密度を 100 (A/m<sup>2</sup>, DC) 又は 50 (A/m<sup>2</sup>, AC) として陽極酸化を行い、アルミニウム板の表面にアルマイト皮膜を形成したことを特徴とする亜鉛-臭素電池用セパレータの製造方法。

【請求項 3】 上記アルミニウム板上に形成されたアルマイト皮膜を逆電剥離法によってバリヤ層直上から分離することにより、多数の細孔が貫通した六角セルを有する多孔質アルマイト皮膜を得て、このアルマイト皮膜を大気中で 850℃以上で略 1 時間加熱処理したことを特徴とする請求項 2 記載の亜鉛-臭素電池用セパレータの製造方法。

【請求項 4】 電解液として硫酸アルミニウムを含有する硫酸を用いるとともに、この硫酸の濃度を 5～25 %、硫酸アルミニウムを 1～50 (kg/m<sup>3</sup>)、温度を 15℃～25℃、電源電圧を 15～20 V (DC)、電流密度を 80～300 (A/m<sup>2</sup>) として陽極酸化を行い、アルミニウム板の表面にアルマイト皮膜を形成したことを特徴とする亜鉛-臭素電池用セパレータの製造方法。

【請求項 5】 電解液として硫酸にスルホサリチル酸を加えた液を用いるとともに、電解液の温度を 22℃～25℃、電源電圧を 25～70 V (DC)、電流密度を 200～3200 (A/m<sup>2</sup>) として陽極酸化を行い、ア \*

充電時……正極： $2\text{Br}^- \rightarrow \text{Br}_2 + 2\text{e}^-$ 、負極： $\text{Zn}^{++} + 2\text{e}^- \rightarrow \text{Zn}$

放電時……正極： $2\text{Br}^- \leftarrow \text{Br}_2 + 2\text{e}^-$ 、負極： $\text{Zn}^{++} + 2\text{e}^- \leftarrow \text{Zn}$

で表される。

【0006】この亜鉛-臭素電池は、主に電極をパイプ型とし、複数個の単電池（単セル）を電気的に直列に積層した電池本体と、電解液貯蔵槽と、これらの間に電解液を循環させるポンプおよび配管系とで構成されている。

【0007】図 6 の概要図に基づいて亜鉛-臭素電池の作動原理を説明する。図中の 1 は正極側貯蔵槽であって該正極側貯蔵槽 1 内に正極電解液 2 と臭素錯化合物 3 とが貯蔵されている。4 は負極側貯蔵槽であって該負極側

\*ルミニウム板の表面にアルマイト皮膜を形成したことを特徴とする亜鉛-臭素電池用セパレータの製造方法。

【請求項 6】 アルミニウム板の陽極酸化すべき面に多数個の丸孔が開孔されたマスクを固着して、電解液中で陽極酸化することによってマスクに覆われていないアルミニウム板の表面部分にアルマイト皮膜を形成し、更にアルミニウム板の上記アルマイト皮膜の形成した面とは逆方向から全面にアルマイト皮膜を形成して該アルマイト皮膜を前記アルマイト皮膜と連結し、マスクで覆われた部分に残存する未反応のアルミニウム板を酸を用いて溶解除去して、得られた部材の 2 枚を用いて各平坦面を背中合わせに連結し、両面に電極板を固着して得たことを特徴とする亜鉛-臭素電池用セパレータの製造方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は電解液循環型積層二次電池、特に亜鉛-臭素電池の構成部材であるセパレータとその製造方法に関するものである。

## 【0002】

【従来の技術】亜鉛-臭素電池は正極活物質に臭素、負極活物質に亜鉛を用いた 2 次電池であり、この電池は例えば電力の昼と夜のアンバランスを解決させるために、電力需要が少ない夜間に電力を貯蔵して、昼間に放出させるため等に使用される。

【0003】充電時に正極電極側で発生した臭素は、電解液に添加した臭素錯化剤と反応し、オイル状の沈殿物となって貯蔵タンクへ戻され、放電時はポンプで単電池内へ送り込まれ還元される。電解液の成分は  $\text{ZnBr}_2$  水溶液と、抵抗を下げるための  $\text{NH}_4\text{Cl}$  等の塩と、負極亜鉛側のデンドライトを防止し、均一な電着を促進させるための  $\text{Pb}$ 、 $\text{Sn}$ 、4 級アンモニウム塩類と、臭素錯化剤とである。正極電極と負極電極の間にはセパレータを介挿してあり、正極電極で発生した臭素が負極電極へ拡散して亜鉛と反応することによる自己放電を防止している。

【0004】この亜鉛-臭素電池の化学反応は、

## 【0005】

## 【化 1】

貯蔵槽 4 内に負極電解液 5 が貯蔵されている。そして正極電解液 2 は正極側ポンプ 6 の駆動に伴って、四方弁 7 を介して図中の矢印に示した如く電池本体の正極マニホール 8 から正極室内を流通し、正極側貯蔵槽 1 に還流する一方、負極電解液 5 は負極側ポンプ 9 の駆動に伴って、電池本体の負極マニホール 10 からセパレータ 11 に隔てられた負極室内を流通して負極側貯蔵槽 4 に還流する。12 は中間電極、13 は集電電極である。

【0008】集電電極 13 の電極材料は、ポリエチレンをバインダーとして導電性を付与するためのカーボン

ラック及びグラファイトを適宜の比率で溶融混合してからシート化したカーボンプラスチック電極材料を用いる。正極には臭素の反応過電圧を減少させるためにカーボクロス又はカーボンファイバーを樹脂バインダーでシート化したものをラミネートさせてある。

【0009】上記セパレータ11は、通常比較的固いポリエチレン樹脂にシリカ及びジオクチルフタレート(DOP)を溶融混合した後、DOPを溶媒で抽出して多孔化してから押出成形手段で得られるた微多孔質膜が用いられている。この微多孔質膜の平均孔径は約 $0.1\mu\text{m}$ ( $1000\text{\AA}$ )程度となっている。

【0010】上記亜鉛-臭素電池は、充電時に正極側で発生した臭素が電解液中に含まれる臭素錯化剤(4級アンモニウム塩)と反応してオイル状の臭素コンプレックスとして正極側タンクの底に貯留され、コンプレックス化されない臭素は、 $\text{Br}_3^-$ イオンとなって電解液に溶解し、亜鉛はカーボンプラスチック電極に電析する。

【0011】このように構成された亜鉛-臭素電池は、50KW級電池における電池効率として約80%、総合エネルギー効率として約70%が確認されている。

【0012】

【発明が解決しようとする課題】このような電力貯蔵用亜鉛-臭素電池の効率は、インバータ効率も含めた総合効率を高めることが要求されるが、効率を阻害する要因の一つにセパレータの孔径制御の問題がある。前記したようにセパレータは多孔質膜であり、 $\text{Zn}^{++}$ イオンと $\text{Br}^-$ イオンは透過しても臭素及び臭素錯化合物は透過しないことが必要である。特に孔径が大きすぎると臭素分子( $\text{Br}_2$ )とか臭素錯化合物( $\text{QBr}_3$ )も多量に透過してしまい、電池の効率が低下してしまうことになる。

【0013】しかし該セパレータの孔径は成形条件によって変化してしまうことが多く、通常のポリエチレン樹脂にシリカをDOPとともに溶融混合した後に押出成形する方法では微細な孔径制御は難しく、且つ一定の孔径で直線状に貫通した孔形状が得られないという問題が残存しており、上記したような選択透過性の良好なセパレータを得ることが困難な現状にある。

【0014】通常、ポリエチレン樹脂を用いたセパレータの孔径は平均 $0.1\mu\text{m}$ ( $1000\text{\AA}$ )であるが、実際には200~500 $\text{\AA}$ 程度が適当であるものと推察される。又、孔はボイド間を縫うように複雑な経路でセパレータ板の表裏間を貫通しているため、孔の実際の行程は板厚よりもかなり長くなっているのが通例である。更にセパレータ板の厚みは約1mmもあるため、電池内にある電解液の膨潤が発生しやすい傾向にある。

【0015】本発明は上記の点に鑑みてなされたものであり、前記セパレータの孔径制御の精度を高めるとともに、孔を直線状に形成することによって実際の行程を短縮して電池効率を高めることができる亜鉛-臭素電池用セパレータとその製造方法を提供することを目的とする

ものである。

【0016】

【課題を解決するための手段】本発明は上記目的を達成するために、中間電極にセパレータを重ねて単セルを形成し、この単セルを複数個積層して電池本体を構成するとともに、該電池本体の両端部に一対の集電電極と締付端板を配置して一体的に積層固定するようにした亜鉛-臭素電池において、前記セパレータとして、アルミニウムを陽極酸化処理して形成されたアルマイト皮膜を用いたことを特徴としている。

【0017】請求項2として、反応槽内に電解液として濃度が3~4%の硫酸を入れ、陽極側に板厚が0.3mm以下のアルミニウム板を浸漬するとともに陰極側に鉛電極を対向して浸漬し、電源のプラス側をアルミニウムに接続するとともに電源のマイナス側を鉛電極に接続して、電解液の温度、電源電圧、電流密度を適宜な値に維持して陽極酸化を行い、アルミニウム板の表面にアルマイト皮膜を形成した亜鉛-臭素電池用セパレータの製造方法を提供する。

【0018】請求項3により、上記アルミニウム板上に形成されたアルマイト皮膜を逆電剥離法によってバリヤ層直上から分離することにより、多数の細孔が貫通した六角セルを有する多孔質アルマイト皮膜を得て、このアルマイト皮膜を大気中で850℃以上、好ましくは略900℃で1時間加熱処理した方法を提供する。

【0019】更に請求項4により電解液として硫酸アルミニウムを含有する硫酸を用いた方法を、請求項5により電解液として硫酸にスルホサリチル酸を加えた液を用いた方法を提供する。

【0020】又、請求項6により、アルミニウム板の陽極酸化すべき面に多数個の丸孔が開口されたマスクを固着して、電解液中で陽極酸化することによってマスクに覆われていないアルミニウム板の表面部分にアルマイト皮膜を形成し、更にアルミニウム板の上記アルマイト皮膜の形成した面とは逆方向から全面にアルマイト皮膜を形成して該アルマイト皮膜を前記アルマイト皮膜と連結し、マスクで覆われた部分に残存する未反応のアルミニウム板を酸を用いて溶解除去して、得られた部材の2枚を用いて各平坦面を背中合わせに連結し、両面に電極板を固着して得た亜鉛-臭素電池用セパレータの製造方法を提供する。

【0021】

【作用】かかるセパレータによれば、アルミニウム板を陽極酸化処理することによって多孔性のアルマイト皮膜が形成され、これを逆電剥離法等によりバリヤ層の直上でアルミニウム板側から分離することによって板厚方向に均一に分散した多数の細孔が貫通した多孔質アルマイト皮膜が得られる。上記陽極酸化時に皮膜に加える電圧によって細孔のサイズが決定されるので、細孔径の制御が容易となる。



【0022】陽極酸化処理したままのアルマイト皮膜はアモルファス状態の $A1_2O_3$ であり、陽極酸化後に加熱処理を行うことによって $\delta-A1_2O_3$ の結晶構造に変態し、強酸性の電解液中での耐食性も大幅に向上する。

【0023】このアルマイト皮膜は板厚方向に細孔が直線状に貫通しており、通常多孔質ポリエチレン膜に比して同一板厚でも孔の行程はかなり短い。且つアルマイト皮膜の厚みは大幅に薄くすることが可能である。

【0024】更に請求項6記載の方法を用いたことにより、セパレータ自体がコンパクト化されるとともに選択透過性の良好な膜が得られ、従来のポリエチレン樹脂の混練作業に比して製造が容易な亜鉛-臭素電池用セパレータを得ることができる。

【0025】

【実施例】以下本発明にかかる亜鉛-臭素電池用セパレータ及びその製造方法の具体的な各種実施例を説明する。本実施例では、アルミニウムを陽極酸化処理して形成されるアルマイト皮膜を選択透過性を有するセパレータとして用いたことが大きな特徴となっている。

【0026】図2は本発明の第1実施例で採用したアルミニウムの陽極酸化装置例であり、図示したように反応槽15内に電解液として稀酸16を入れて、陽極側にアルミニウム板17を、陰極側に鉛電極18を対向して浸漬し、電源19のプラス側をアルミニウム板17に接続するとともに電源19のマイナス側を鉛電極18に接続し、適宜な温度と電圧を維持しながら反応を行わせることにより、アルミニウム板17の表面に陽極酸化皮膜、即ちアルマイト皮膜20が形成される。

【0027】本実施例では、上記稀酸法による多孔質のアルマイト皮膜20の成膜条件として、アルミニウム板17の化学組成が、 $Al99.99\%$ 以上、板厚は $0.3\text{ mm}$ 以下とし、稀酸16の濃度は $3\sim4\%$ 、電解液の温度は $20^\circ\text{C}\sim30^\circ\text{C}$ 、電源19の電圧を $25\text{ V (DC)}$ 又は $80\text{ V (AC)}$ 、電流密度を $100\text{ (A/m}^2\text{, DC)}$ 又は $50\text{ (A/m}^2\text{, AC)}$ とした。

【0028】得られたアルマイト皮膜20は、直流電圧では透明であるが、交流電圧では淡黄～褐色を呈した。

【0029】図1は得られた多孔質なアルマイト皮膜20の構造を示す概要図であり、アルミニウム板17上に形成されたアルマイト皮膜20を逆電剥離法によってバリヤ層21直上の点線部22でアルミニウム板17側から分離することにより、上下に細孔23、23が貫通した六角セル24を有する厚さ $t$ が $80\text{ }\mu\text{m}$  (最大 $400\text{ }\mu\text{m}$ )、細孔径 $40\text{ nm}$  ( $400\text{ }\text{\AA}$ )の多孔質アルマイト皮膜を得た。このアルマイト皮膜20を大気中で $90^\circ\text{C}$ 、1時間加熱処理した。

【0030】従って本第1実施例では、アルミニウム板17を稀酸法で陽極酸化処理することにより、多孔性のアルマイト皮膜20を最大 $400\text{ }\mu\text{m}$ の厚さまで成長させることが可能であり、これを逆電剥離法等によりバリ

ヤ層21の直上でアルミニウム板17側から分離することによって板厚方向に多数の細孔23、23が貫通した多孔質アルマイト皮膜20が得られる。

【0031】上記陽極酸化処理時に皮膜に加える電圧によって上記六角セル24のサイズ、細孔23、23のサイズが決定される。電圧を $V$ とすると、六角セル24のサイズ直径 $D_c(2R)$ は、 $D_c=23\times V(\text{\AA})$ であり、細孔23、23のサイズ直径 $D_p(2r)$ は、 $D_p=D_c/3(\text{\AA})$ である。

10 【0032】本実施例で得られたアルマイト皮膜20を $\text{pH}1$ の強酸性電池用電解液中に浸漬して、 $1500$ 時間(約2カ月)経過しても溶解せずに原形が保持された。

【0033】図3(A)(B)は本実施例で得られたアルマイト皮膜20のX線回析による分析結果を示すスペクトルであり、同図(A)は未加熱のもの、同図(B)は大気中で $900^\circ\text{C}$ 、1時間加熱処理したものである。図3から陽極酸化処理したままのアルマイト皮膜20はアモルファス状態の $A1_2O_3$ であり、陽極酸化処理後に加熱処理を行うことによって $\delta-A1_2O_3$ の結晶構造に変態したことが判明した。

【0034】図4はアルマイト皮膜20の熱重量測定(TG)結果を示すスペクトルであり、同図から温度上昇に伴って皮膜表面に吸着していた水分の放出による重量漸減が認められ、 $850^\circ\text{C}$ 付近でアモルファス状態から $\delta-A1_2O_3$ 結晶への変態に対応すると考えられる大幅な重量減が認められた。これは水和物からの結晶水の分解放出や微量含まれている $Al(OH)_3$ からのOH基の分解放出に起因するものと考えられる。

30 【0035】つまり水分を吸着したことによって結晶水や $Al(OH)_3$ を一部含んだアモルファス状態の $A1_2O_3$ から成るアルマイト皮膜20は、 $900^\circ\text{C}$ の高温加熱処理によって $\delta-A1_2O_3$ 結晶上に変態し、強酸性の電解液中での耐食性も大幅に向上していることが判明した。

【0036】現状の多孔質ポリエチレン膜セパレータの孔径が平均 $0.1\text{ }\mu\text{m}$  ( $1000\text{ }\text{\AA}$ )であるのに比して、稀酸法によるアルマイト皮膜は、加える電圧によって約 $200\text{ }\text{\AA}\sim500\text{ }\text{\AA}$ の範囲内で細孔径の制御が可能であり、この細孔径の制御が容易となる。得られた細孔径も小さく、且つ細孔が均一に分散している。

【0037】又、稀酸法によるアルマイト皮膜は板厚方向に細孔が直線状に貫通しているため、現状の多孔質ポリエチレン膜、即ち、多数のボイド間を縫うようにして複雑な経路で細孔が貫通している膜に比して同一板厚でも孔の行程はかなり短い。

【0038】更に稀酸アルマイト皮膜は多孔質ポリエチレン皮膜に比して板厚を大幅に薄くすることができる。現状のポリエチレン膜の厚さは約 $1\text{ mm}$ であるのに対して本実施例の稀酸アルマイト皮膜の厚さは約 $30\sim40$

0 μm の範囲で任意の皮膜作成が可能である。

【0039】本第1実施例によって成膜したアルマイト皮膜は水分を吸着しやすく、結晶水とか  $\text{Al}(\text{OH})_3$  を一部含んだアモルファス状態の  $\text{Al}_2\text{O}_3$  で強酸性の電解液中で2、3日の短時間で溶解してしまうが、850℃以上、好ましくは900℃で1時間の高温加熱処理をほって  $\delta\text{-Al}_2\text{O}_3$  結晶に変態し、耐食性を大幅に改善することができる。但し単一のアルマイト皮膜では大面積化が困難であって、通常は5×5cm程度が限界である。

【0040】次に本発明の第2実施例を説明する。この第2実施例では、前記第1実施例でアルマイト皮膜を形成する際に使用した電解液としての蔭酸に代えて、硫酸を用いたことを特徴としている。尚、図2に示したアルミニウムの陽極酸化装置は蔭酸16を硫酸に変更しただけで他の部分は同一である。この硫酸中には所定量の硫酸アルミニウムが含有されている。

【0041】この硫酸法による多孔質なアルマイト皮膜20の成膜条件として、アルミニウム板17の化学組成は、 $\text{Al}99.99\%$ 以上、板厚は0.3mm以下とし、電解液としての硫酸の濃度は5～25%、硫酸アルミニウムは1～50 ( $\text{kg}/\text{m}^3$ )、電解液の温度は15℃～25℃、電源電圧を15～20V (DC)、電流密度は80～300 ( $\text{A}/\text{m}^2$ )とした。この硫酸法によって得られたアルマイト皮膜20は、無色透明を呈した。

【0042】第2実施例で得られた多孔質なアルマイト皮膜20の構造は図1と同一であり、逆電剥離法によってバリヤ層21直上の点線部22でアルミニウム板17側から分離することにより、上下に細孔23、23が貫通した六角セル24を有する厚さtが30 μm～300 μm、細孔径100 Å～250 Åの範囲にある多孔質アルマイト皮膜を得た。このアルマイト皮膜20を大気中で900℃、1時間加熱処理した。

【0043】陽極酸化処理時に皮膜に加える電圧によって上記六角セル24のサイズ、細孔23、23のサイズが決定されることは前記実施例1と同様であり、得られたアルマイト皮膜20をpH1の強酸性電池用電解液中に浸漬して、1500時間(約2カ月)経過しても溶解せずに原形が保持された。

【0044】この第2実施例で得られたアルマイト皮膜20のX線回析による分析結果をみると、陽極酸化処理したままのアルマイト皮膜20はアモルファス状態の  $\text{Al}_2\text{O}_3$  であり、陽極酸化処理後に加熱処理を行うことによって  $\delta\text{-Al}_2\text{O}_3$  の結晶構造に変態したことが判明した。更に熱重量測定(TG)結果を示すスペクトルによれば、温度上昇に伴って皮膜表面に吸着していた水分の放出による重量漸減が認められ、890℃付近でアモルファス状態から  $\delta\text{-Al}_2\text{O}_3$  結晶への変態に対応すると考えられる大幅な重量減が認められた。

【0045】次に本発明の第3実施例を説明する。この

第3実施例では、アルマイト皮膜を作成する際カルカラー法を用いたことを特徴としている。このカルカラー法では電解液として硫酸50 ( $\text{kg}/\text{m}^3$ ) にスルホサリチル酸100 ( $\text{kg}/\text{m}^3$ ) を加えた液を用いており、電解液の温度は22℃～25℃、電源電圧を25～70V (DC)、電流密度は200～3200 ( $\text{A}/\text{m}^2$ )とした。このカルカラー法によって得られたアルマイト皮膜20は、ブロンズ～黒色を呈した。

【0046】尚、図2に示したアルミニウムの陽極酸化装置は電解液を変更しただけで他の部分は同一である。このカルカラー法による多孔質なアルマイト皮膜20の成膜条件として、アルミニウム板17の化学組成として  $\text{Al}99.99\%$ 以上、板厚は0.3mm以下とした。

【0047】得られた多孔質なアルマイト皮膜20の構造は図1と同一であり、逆電剥離法によってバリヤ層21直上の点線部22でアルミニウム板17側から分離することにより、上下に細孔23、23が貫通した六角セル24を有する厚さtが30 μm～400 μm、細孔径200 Å～600 Åの多孔質アルマイト皮膜を得た。このアルマイト皮膜20を大気中で900℃、1時間加熱処理した。

【0048】陽極酸化処理時に皮膜に加える電圧によって上記六角セル24のサイズ、細孔23、23のサイズが決定されることは前記実施例1と同様であり、得られたアルマイト皮膜20をpH1の強酸性電池用電解液中に浸漬して、1500時間(約2カ月)経過しても溶解せずに原形が保持された。

【0049】この第3実施例で得られたアルマイト皮膜20のX線回析による分析結果をみると、陽極酸化処理したままのアルマイト皮膜20はアモルファス状態の  $\text{Al}_2\text{O}_3$  であり、陽極酸化処理後に加熱処理を行うことによって  $\delta\text{-Al}_2\text{O}_3$  の結晶構造に変態したことが判明した。更に熱重量測定(TG)結果を示すスペクトルによれば、温度上昇に伴って皮膜表面に吸着していた水分の放出による重量漸減が認められ、860℃付近でアモルファス状態から  $\delta\text{-Al}_2\text{O}_3$  結晶への変態に対応すると考えられる大幅な重量減が認められた。

【0050】図5は本発明の第5実施例を示しており、この実施例は上記各実施例で説明したアルマイト皮膜20の形成方法を利用して、亜鉛-臭素電池用セパレータ11を製作した具体例を示している。

【0051】以下工程順に基づいて説明すると、先ず同図(A)のように厚さ0.8mmのアルミニウム板17の陽極酸化すべき面に多数個の丸孔が開口されたマスク25を固着して、このマスク25が固着された面を内側として反応槽15の底部に陽極としてセットし、電解液として蔭酸16を入れるとともに陰極側に鉛電極18を対向配置し、電源19のプラス側をアルミニウム17に接続するとともに電源19のマイナス側を鉛電極18に接続する。そして前記第1実施例で開示した温度と電圧

及び電流密度を維持しながら陽極酸化反応を行わせると、マスク 25 に覆われていないアルミニウム板 17 の表面部分にアルマイト皮膜 20、20a が形成される。尚、このアルマイト皮膜 20、20a の厚みは 0.4 mm とする。

【0052】次に同図 (B) に示したように、アルミニウム板 17 の上下を反転して、上記アルマイト皮膜 20 が形成された面とは逆方向から同様の操作に基づいて全面にアルマイト皮膜 20a を形成する。このアルマイト皮膜 20a の厚みは前記と同様に 0.4 mm とする。

【0053】この工程によってアルマイト皮膜 20 とアルマイト皮膜 20a とが上下から連結して、マスク 25 で覆われた部分に未反応のアルミニウムの島 17a、17a が残るので、同図 (C) に示したように塩酸 27 を満たした容器 28 内に全体を浸漬して未反応のアルミニウム板 17 を溶解除去する。26 はアルミニウムの除去部分であり、アルマイト皮膜 20、20a を主体とする部分は溶解されずに塩酸 27 中に残存する。尚、この後に水酸化ナトリウム溶液に浸漬してバリヤ層を除去する。

【0054】同図 (D) (E) は得られたアルマイト皮膜によって構成したセパレータ 11 の構造を示すものであって、上記によって得られたアルマイト皮膜 20、20a で構成された部材を 2 枚用いて、両部材の平坦面を背中合わせに連結し、左右両面に電極板 29、29 を固着して完成する。この時に空孔部 30 は電解液の流路となる。

【0055】この第 5 実施例によれば、セパレータ 11 自体がコンパクト化されるとともに選択透過性の良好な膜が得られ、且つ従来のポリエチレン樹脂の混練作業に比して工程自体が簡略化されて製造が容易な亜鉛-臭素電池用セパレータを得ることができる。

【0056】

【発明の効果】以上詳細に説明したように、本発明にかかる亜鉛-臭素電池用セパレータによれば、アルミニウム板を陽極酸化処理することによって得られた多孔性のアルマイト皮膜を材料とするセパレータを実現したことにより、陽極酸化時に皮膜に加える電圧によって細孔のサイズが決定されるので、細孔径の制御が容易となって従来から電池効率を阻害する要因の一つとされているセパレータの微細な孔径制御の精度が向上し、一定の孔径で直線状に貫通した孔形状が得られて、選択透過性が良好で電池効率を高めることができるセパレータが得られる。

【0057】上記の細孔は板厚方向に均一に分散してお

り、しかも直線状に貫通しているので、通常の多孔質ポリエチレン膜に比して同一板厚でも孔の行程はかなり短くなり、且つアルマイト皮膜の厚みは大幅に薄くすることが可能である。

【0058】更に請求項 6 記載の方法を用いたことにより、セパレータ自体がコンパクト化されるとともに従来のポリエチレン樹脂の混練作業に比して製造が容易な亜鉛-臭素電池用セパレータを得ることができる。

【図面の簡単な説明】

10 【図 1】本実施例で得られた多孔質アルマイト皮膜の構造を示す概要図。

【図 2】本実施例で採用したアルミニウムの陽極酸化装置例を示す概略断面図。

【図 3】本実施例で得られたアルマイト皮膜の X 線回析による分析結果を示すスペクトル。

【図 4】本実施例で得られたアルマイト皮膜の熱重量測定 (TG) 結果を示すスペクトル。

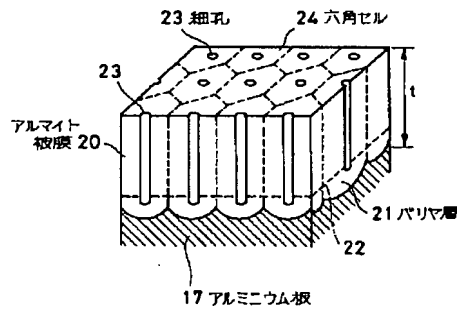
20 【図 5】本実施例にかかるアルマイト皮膜の形成方法を利用して亜鉛-臭素電池用セパレータを製作した具体例を示す概要図。

【図 6】亜鉛-臭素電池の作動原理を説明する概要図。

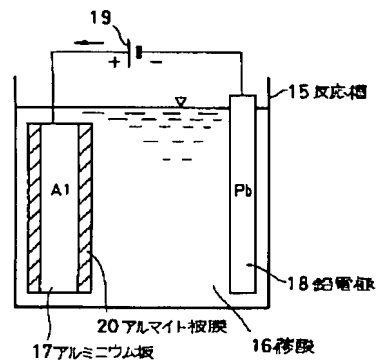
【符号の説明】

- 1…正極側貯蔵槽
- 2…正極電解液
- 3…臭素錯化合物
- 4…負極側貯蔵槽
- 5…負極電解液
- 6…正極側ポンプ
- 7…四方弁
- 30 8…正極マニホールド
- 9…負極マニホールド
- 11…セパレータ
- 12…中間電極
- 13…集電電極
- 15…反応槽
- 16…蔭酸
- 17…アルミニウム板
- 18…鉛電極
- 19…電源
- 40 20…アルマイト皮膜
- 21…バリヤ層
- 23…細孔
- 24…六角セル
- 25…マスク
- 29…電極板

【図1】

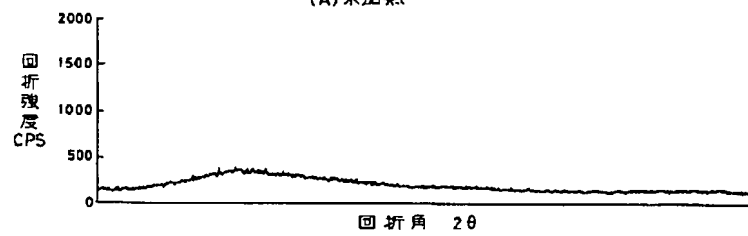


【図2】

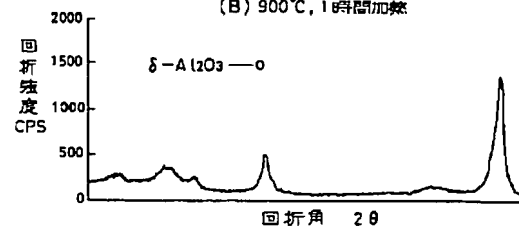


【図3】

X線回折スペクトル  
(A) 未加熱

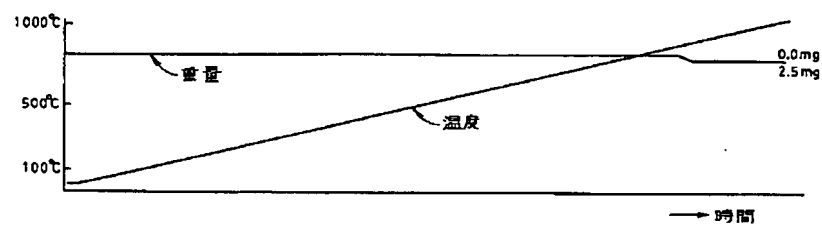


(B) 900℃, 1時間加熱

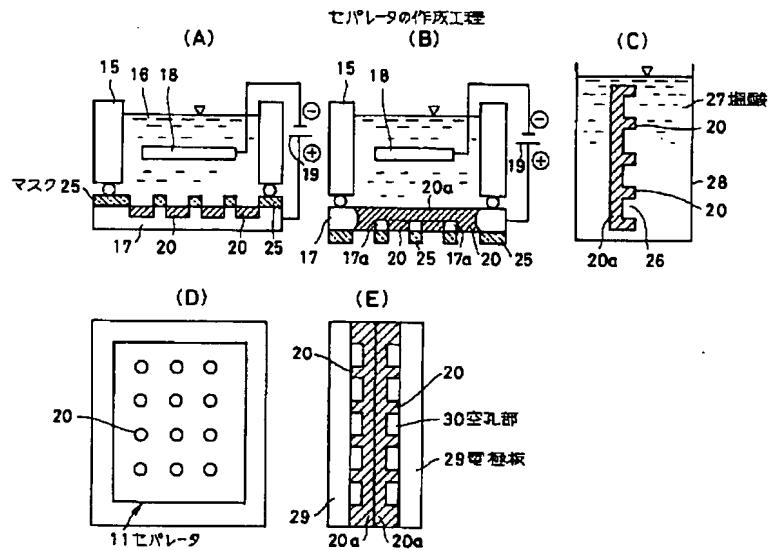


【図4】

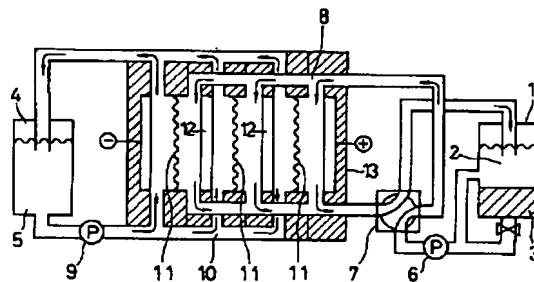
熱重量測定 (TG) スペクトル



【図 5】



【図 6】



- 1 …正極側貯蔵槽
- 2 …正極電解液
- 3 …臭素錯化合物
- 4 …負極側貯蔵槽
- 5 …負極電解液
- 7 …四方弁
- 8 …正極マニホールド
- 10 …負極マニホールド
- 11 …セパレータ
- 12 …中間電極
- 13 …集電電極

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